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Synthesis and photophysical studies of novel 4-aryl substituted 2-phenyl-, 2-(fluoren-2-yl)- and 2-cymantrenylquinazolines

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Experimental

Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on the instrument Boetius. ^{1}H NMR spectra were recorded with the Bruker DRX-400 spectrometer using Me_4Si as an internal standard. Mass spectra were recorded on the SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. Microanalyses (C, H, N) were performed using the Perkin–Elmer 2400 elemental analyzer. The absorption spectra were recorded in the interval 220–800 nm on a UV–2600 (Shimadzu, λ = 310 nm). The emission spectra were registered by means of a Varian Cary Eclipse fluorimeter (75 kW xenon lamp).

The single crystal (light yellow prism, 0.25×0.2×0.15 mm) of compound **3b** ($C_{32}H_{21}N_3$) was used for X-ray analysis. Analysis was performed at T= 295(2) K on an Xcalibur 3 diffractometer using graphite monochromated CuKα irradiation (λ= 1.54184 Å) and CCD detector. An empirical absorption correction was applied (μ = 0.542 mm^{-1}). Crystal is triclinic space group P1 with a= 9.008(6), b= 9.415(9) and c= 22.97(2) Å, α= 85.33(7), β= 86.14(6), γ= 76.88(6)^o, V = 1889(3) Å^3, Z = 3. On the angles 3.87 < θ < 67.11^0 21883 reflections were measured, among them 6459 unique reflections (R_{int} = 0.0435), 4491 reflections with I>=2σ(I). Completeness to θ = 67.1088 is 95.52%. The structure was solved by direct method and refined by full-matrix least squares at F^2 using the SHELXTL program package[1]. All non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms were calculated as a riding model in isotropic approximation. Goodness to fit at F^2 1.0188; final R values [I>2σ(I)], R_1 = 0.0505, wR_2 = 0.1292; R value (all reflections) R_1=0.0633, wR_2= 0.1339. Largest difference peak and hole were 0.1943 and -0.2300 e Å^{-3}.

CCDC 1547817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* http://www.ccdc.cam.ac.uk.

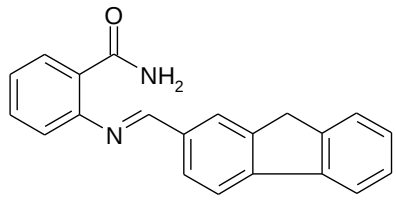
Synthesis of starting 4-bromoquinazolines (2)

4-Bromo-2-phenylquinazoline (2a). To a suspension of 2-phenylquinazolin-4(3*H*)-one **1a** (0.7 g, 3.2 mmol) in toluene (14 ml), trimethylamine (0.35 ml) and solution of $POBr_3$ (3.6 g, 12.5 mmol) in toluene (7.5 ml) were added. The reaction mixture was stirred at 80 °C for 12 h, and then cooled. The precipitate was filtered off, the filtrate was discarded, and product **2a** was extracted from the precipitate

[1] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

with chloroform. The extract was washed with water (2×10 ml), dried over Na_2SO_4 and then concentrated. The residue was recrystallized from hexane to give colorless solid of **2a**. Yield 0.27 g (30%), mp 123-125 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 7.55 (m, 3H), 7.80 (m, 1H), 8.07 (m, 2H), 8.21 (m, 1H, H-8), 8.55 (m, 2H). MS (m/z, I_{rel} %): 286 $[M+2]^+$ (20), 284 $[M]^+$ (21), 206 (16), 205 $[M-Br]^+$ (100), 103 (17), 102 (35), 77 (39), 76 (20), 75 (19), 51 (14). Calcd for $C_{14}H_{10}N_2O$: C 58.97; H 3.18; N 9.82. Found: C 59.05; H 3.16; N 9.80.

2-{*N*-[(Fluoren-2-yl)methylidene]amino}benzamide. To a solution of 2-aminobenzamide (1 g, 7.3 mmol) in ethanol (20 ml), fluorene-2-carbaldehyde (1.4 g, 7.3 mmol) was added. The mixture was refluxed for 3 h, after cooling light yellow precipitate was filtered off and washed with diethyl ester. Yield 2.05 g (89%), mp 233-235 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 3,49 (s, 2H, CH_2), 5.84 (s, 1H, CH), 6.67 (t, 1H, J=7.5), 6.75 (d, 1H, J=7.9), 6.91 (s, 1H, NH_2), 7.20 (t, 1H, J=7.7), 7.30 (t, 1H, J=7.3), 7.36 (t, 1H, J=7.3), 7.55 (t, 2H, J=8.4 Hz), 7.64 (d, 1H, J=7.7 Hz), 7.74 (s, 1H, H-1'), 8.02 (s, 1H, NH_2), Calcd for $C_{21}H_{16}N_2O$: C 80.75; H 5.16; N 8.97. Found: C 80.71; H 5.19; N 8.89.



intermediate to **1b**

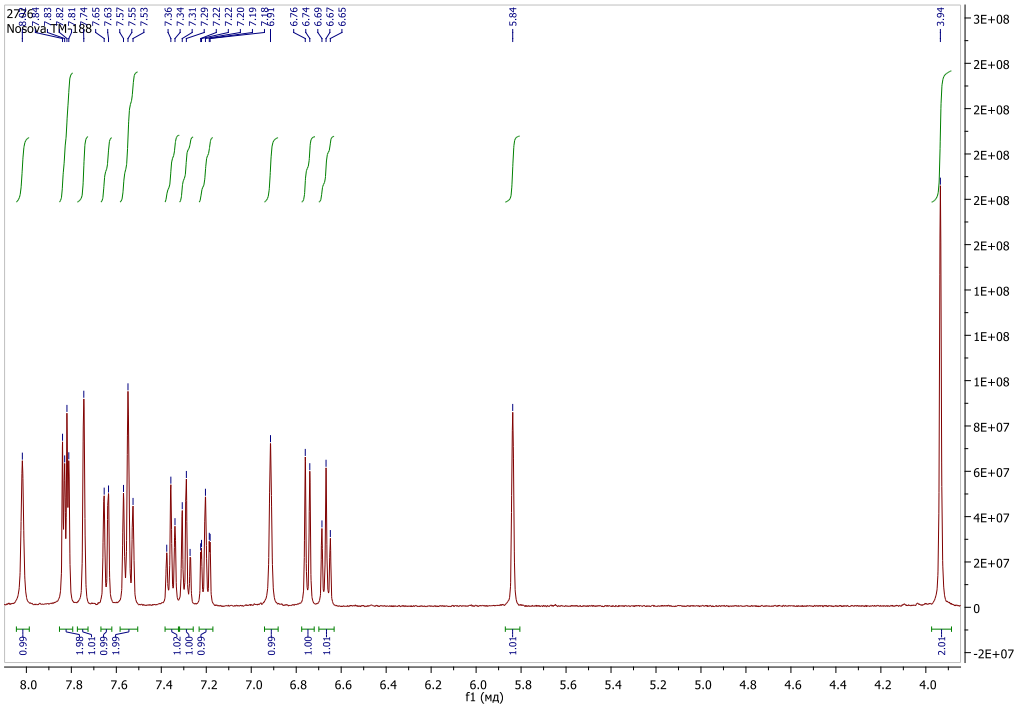
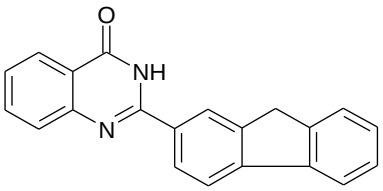


Figure S1. NMR ^{1}H spectrum of 2-{N-[(fluoren-2-yl)methylidene]amino}benzamide in DMSO-d_6.

2-(Fluoren-2-yl)quinazolin-4(3*H*)-one (1b). To a solution of 2-{N-[(fluoren-2-yl)methylidene]amino}benzamide (2.02 g, 6.5 mmol) in ethanol (33 ml), $CuCl_2$ (0.96 g, 7.1 mmol) was added. The mixture was refluxed for 5 h, after cooling the precipitate was filtered off and recrystallized from DMSO. Yield 1.7 g (85%), mp >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 4,03 (s, 2H, CH_2), 7.35 (m, 1H), 7.41 (t, 1H, J=7.3), 7.46 (m, 1H), 7.61 (d, 1H, J=7.5 Hz), 7.72 (d, 1H, J=7.9 Hz), 7.78 (m, 1H),

7.91 (d, 1H, J=7.9 Hz), 7.96 (d, 1H, J=8.1 Hz), 8.16 (m, 1H), 8.29 (m, 1H), 8.48 (s, 1H, H-1'), 12.40 (s, 1H, NH), Calcd for $C_{21}H_{14}N_2O$: C 81.27; H 4.55; N 9.03. Found: C 81.19; H 4.57; N 9.99.



1b

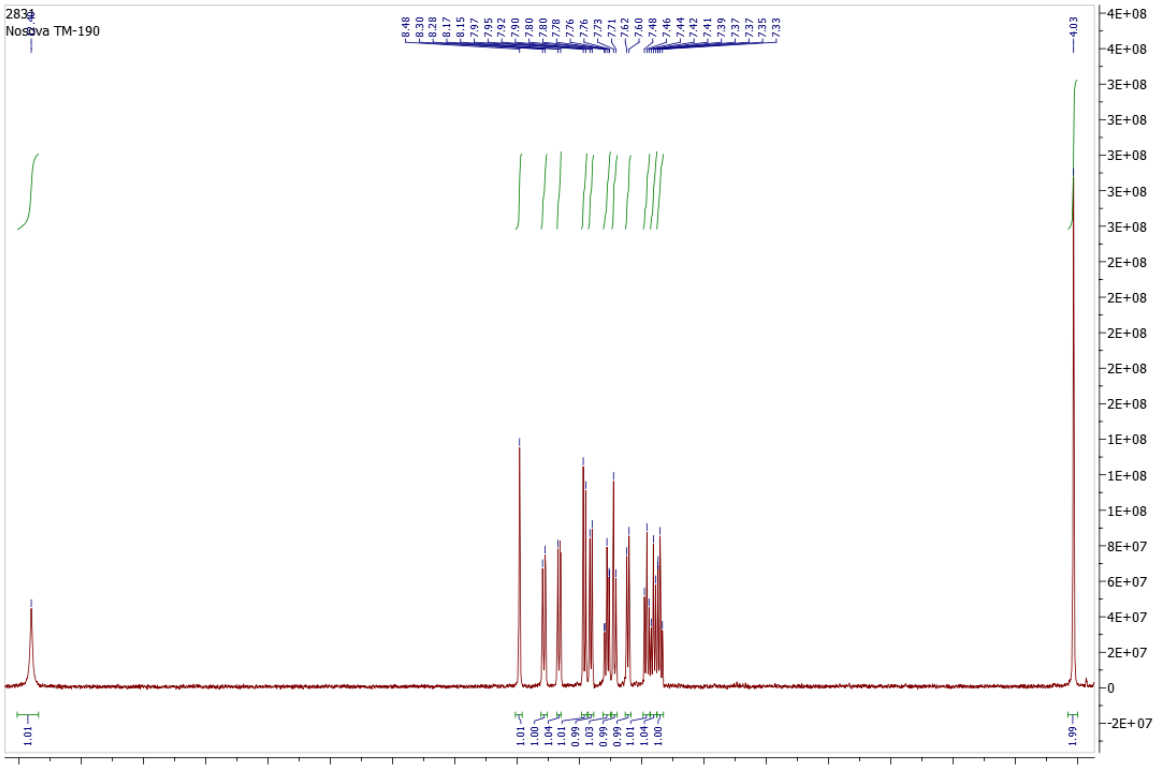
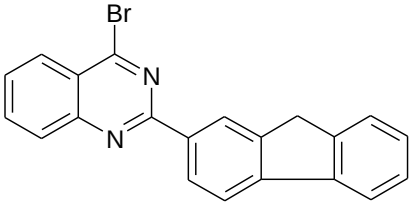


Figure S2. NMR ^{1}H spectrum of quinazolinone **1b** in DMSO-d_6.

4-Bromo-2-(fluoren-2-yl)quinazoline (2b) was obtained by the same method as **1b**. Yield 45%, mp 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 4,06 (s, 2H, CH_2),7.39 (m, 1H), 7.45 (t, 1H, J 7.5 Hz), 7.63 (d, 1H), 7.69 (m, 1H), 7.90 (d, 1H, J 7.8 Hz), 7.96 (m, 2H), 8.11 (d, 1H, J 8.4 Hz), 8.23 (d, 1H, J 8.4 Hz), 8.69 (d, 1H, J 8.2 Hz), 8.81 (s, 1H, H-1'). Calcd for $C_{21}H_{13}BrN_2$: C 67.58; H 3.51; N 7.51. Found: C 67.53; H 3.58; N 7.48.



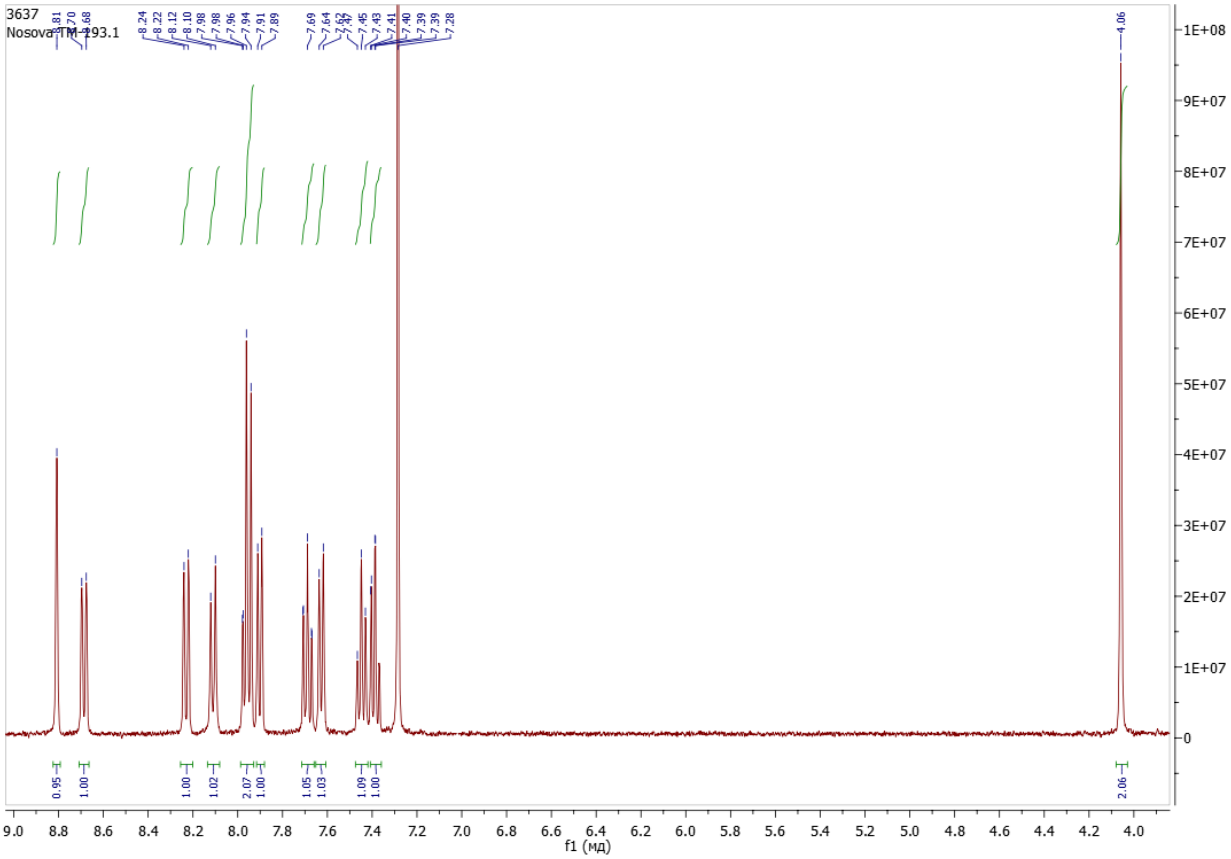


Figure S3. NMR ^{1}H spectrum of quinazoline **2b** in $CDCl_3$.

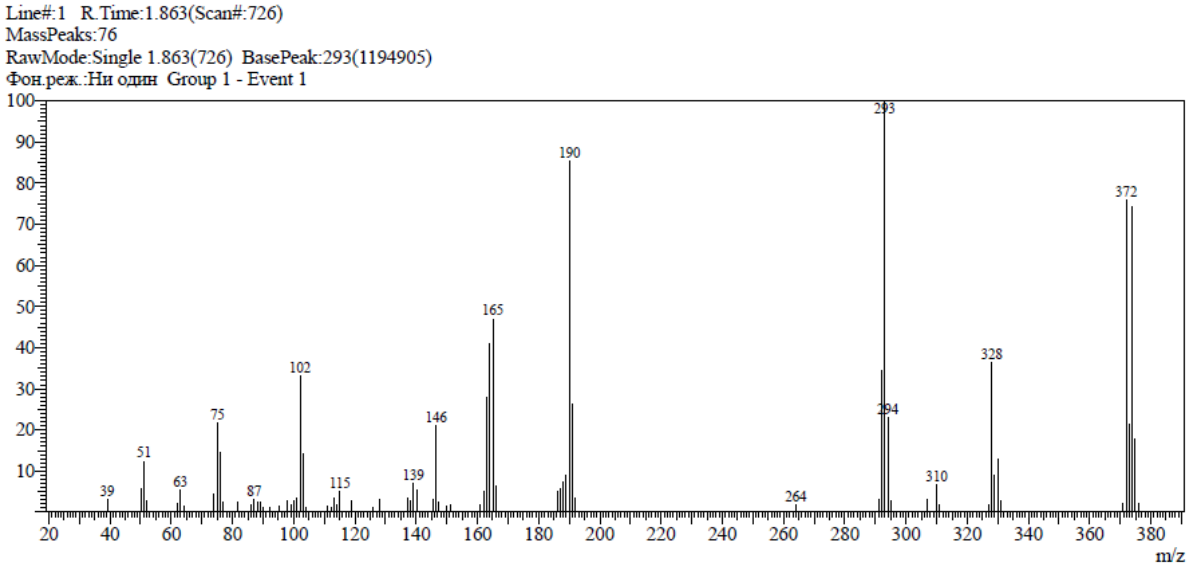
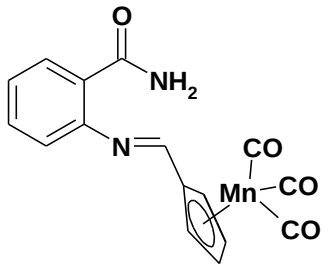


Figure S4. Mass spectrum (EI) of quinazoline **2b.**

2-(Cymantrenylmethylideneamino)benzamide. To a solution of 2-aminobenzamide (1 g, 7.3 mmol) in ethanol (13 ml), formylcymantrene (1.69 g, 7.7 mmol) was added. The mixture was refluxed for 3 h. After cooling the mixture was concentrated under reduced pressure, and diethyl ether (10 ml) was added to the residue. Light-yellow precipitate was filtered off and washed with diethyl ether. Yield 1.16 g (45%), mp 196-198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 5.15 (m, 2H, Cp), 5.74 (m, 2H, Cp), 7.05 (m, 1H, H-3) 7.32 (m, 1H, H-5), 7.39 (s, 1H, NH_2), 7.51 (m, 1H, H-4), 8.00 (m, 1H, H-6), 8.15 (s,

1H, NH_2), 8.28 (s, 1H, CH). Calcd for $C_{16}H_{11}N_2O_4Mn$: C 54.87; H 3.17; N 8.00. Found: C 55.02; H 3.15; N 7.89.



intermediate to **1c**

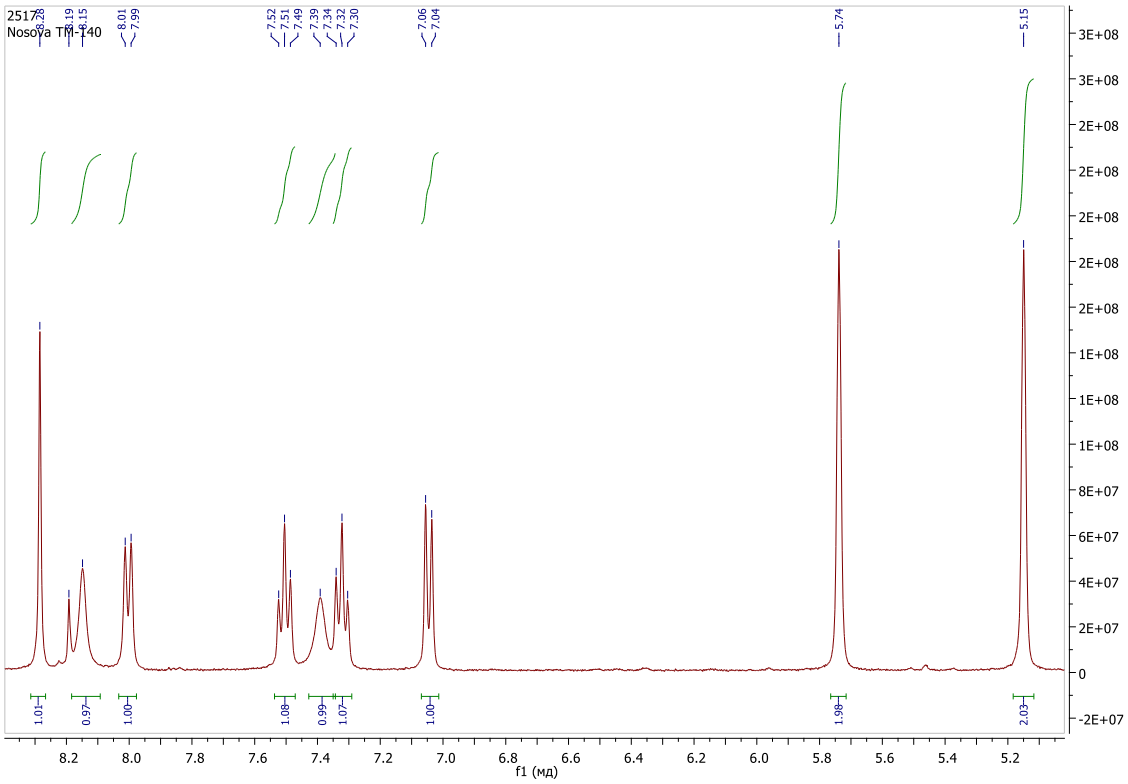
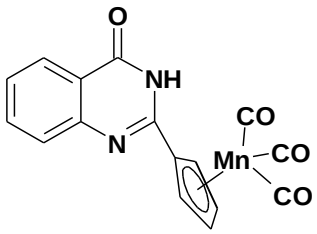


Figure S5. NMR ^{1}H spectrum of 2-(cymantrenylmethylideneamino)benzamide in DMSO-d_6.

2-Cymantrenylquinazolin-4(*3H*)-one (1c). To a suspension of 2-(cymantrenylmethylidene-amino)benzamide (1.16 g, 3.3 mmol) in ethanol (15 ml), copper (II) chloride (0.74 g, 5.5 mmol) was added. The mixture was refluxed for 5 h, after cooling light-yellow precipitate was filtered off and washed with hot ethanol (5 ml). Yield 1.15 g (96 %), mp 262-264 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 5.11 (m, 2H, Cp), 5.13 (m, 2H, Cp), 7.46 (m, 1H, arom.), 7.60 (d, 1H, H-5, J 8.0 Hz), 7.76 (m, 1H, arom.), 8.10 (d, 1H, H-8, J 8.0 Hz), 12.29 (s 1H, NH). MS (m/z, I_{rel} %): 348 $[M]^+$ (9), 292 (9), 265 (15),

264 (100), 172 (44), 55 (46). Calcd for $C_{16}H_9N_2O_4Mn$: C 55.19; H 2.61; N 8.05. Found: C 54.98; H 2.49; N 8.12.



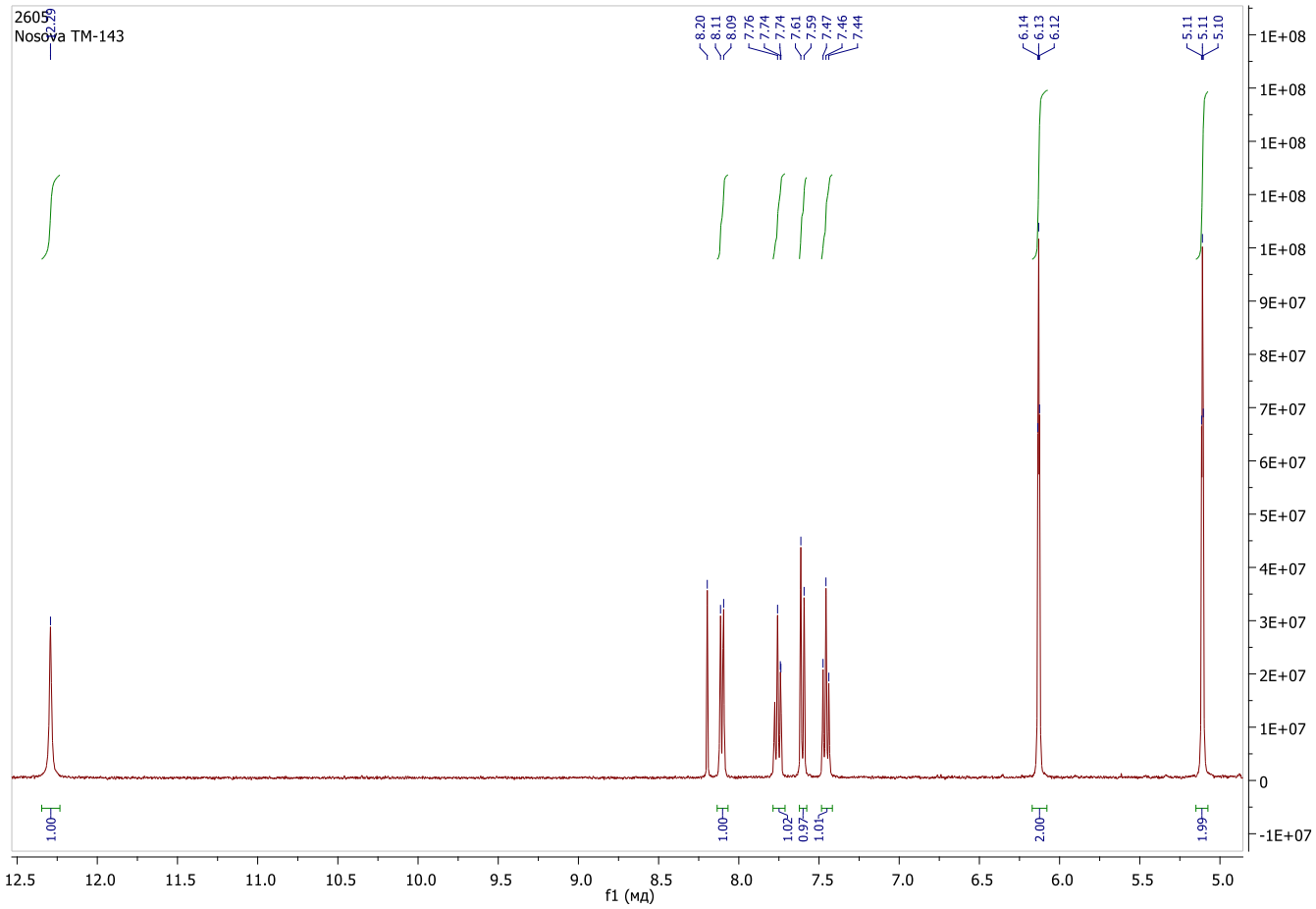


Figure S6. NMR ^{1}H spectrum of quinazolinone **1c** in DMSO-d_6.

4-Bromo-2-cymantrenylquinazoline (2c) was obtained by the same method as 4-bromo-2-phenylquinazoline **2a.** Yield 0.136 g (23%), mp 124-126 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 5.14 (m, 2H, Cp), 5.95 (m, 2H, Cp), 7.79 (m, 1H, H-6), 7.97 (m, 1H, H-5), 8.04 (m, 1H, H-7), 8.17 (m, 1H, H-8). MS (m/z, I_{rel} %): 412 $[M+2]^+$ (12), 410 $[M]^+$ (12), 329 (15), 328 $[M+2-3CO]^+$ (100), 327 (17), 326 $[M-3CO]^+$ (97), 247 (15), 246 $[M-Br-3CO]^+$ (97), 192 (13), 166 (13), 164 (11), 140 (12), 139 (11), 136 (29), 134 (31), 102 (10), 55 (81). Calcd for $C_{16}H_8N_2O_3BrMn$: C 46.75; H 1.96; N 6.81. Found: C 46.61; H 2.07; N 6.34.

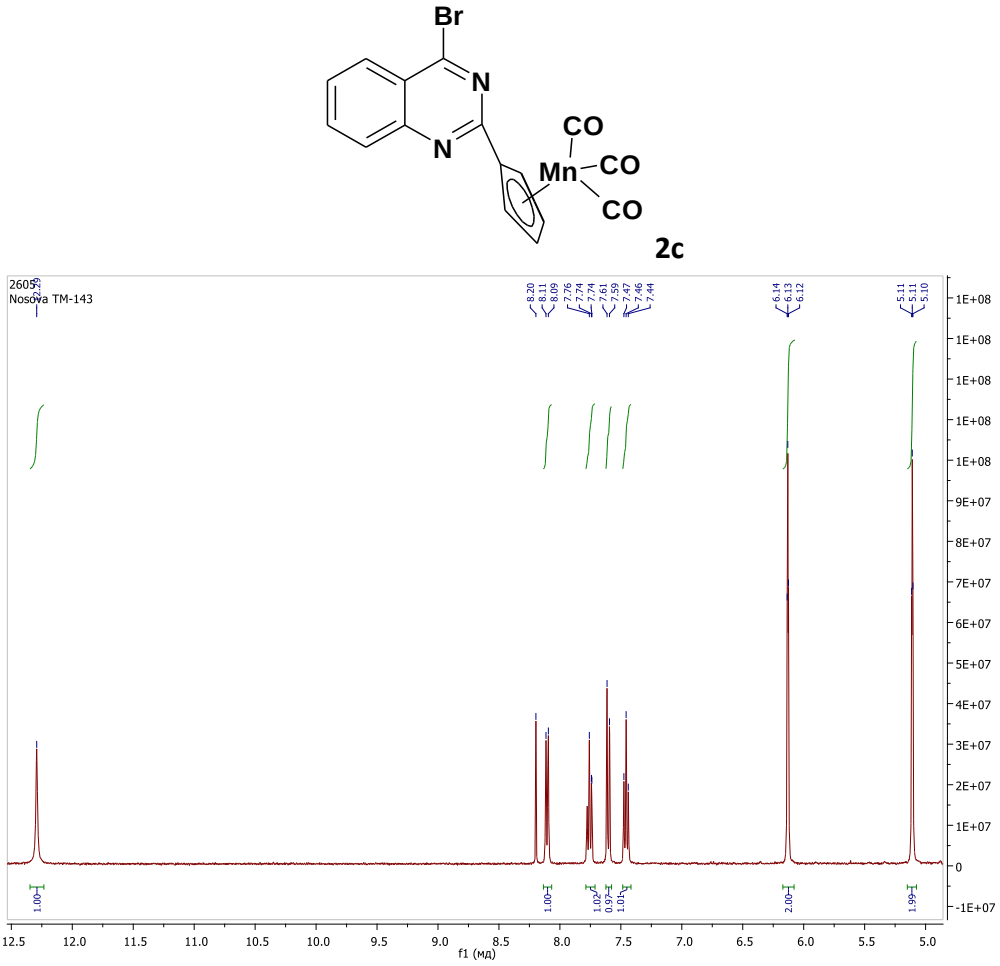


Figure S7. NMR ^{1}H spectrum of quinazoline **2c** in DMSO-d_6.

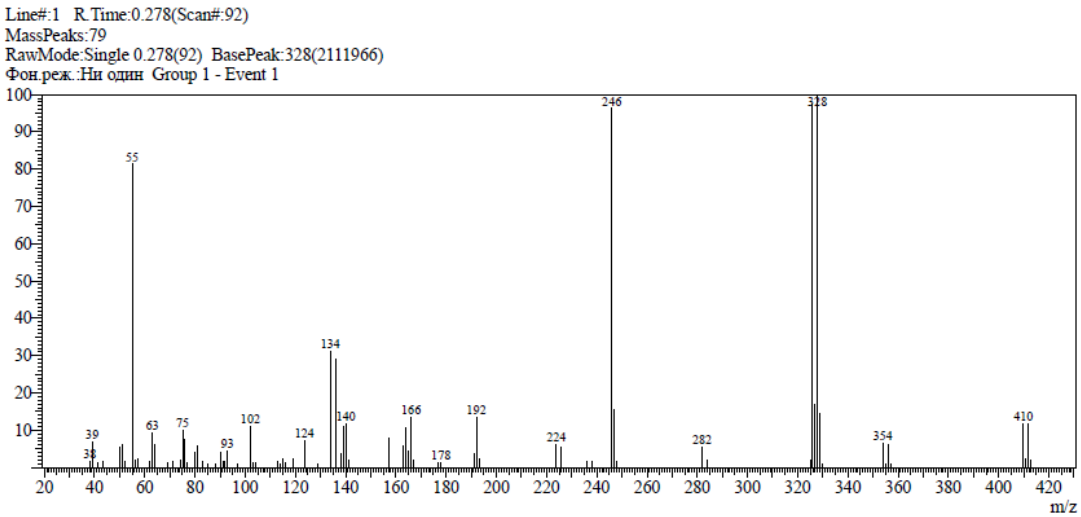
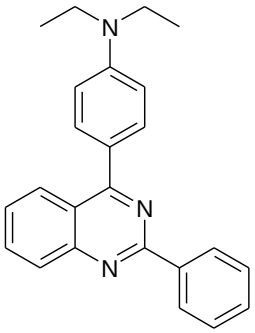


Figure S8. Mass spectrum (EI) of quinazoline **2c.**

4-(4-Diethylaminophenyl)-2-phenylquinazoline (3a). A suspension of bromo quinazoline **2a** (0.047 g, 0.16 mmol) in toluene (4 ml) was stirred at room temperature for 5 min, then 4-diethylamino-phenylboronic acid (0.03 g, 0.156 mmol), $PdCl_2(PPh_3)_2$ (2.88 mg), PPh_3 (2.0 mg), solution of K_2CO_3 (0.18 g, 1.3 mmol) in water (1.4 ml) and ethanol (1.6 ml) were added. The mixture was stirred at 85 °C for 7 h in argon atmosphere. After cooling, the organic layer was separated, washed with saturated solution of K_2CO_3 (15 ml), then with saturated solution of NH_4Cl (15 ml) and dried over Na_2SO_4. The solution was evaporated under reduced pressure and the residue was washed with hexane (10 ml). Yield 0.03 g (53%), mp 105-108 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 1.25 (m, 6H, 2 CH_3), 3.52 (m, 4H, 2 CH_2), 7.50-7.60 (m, 6H), 7.85-7.92 (m, 3H), 8.06 (m, 1H), 8.16 (m, 1H), 8.24 (m, 1H), 8.64 (m, 2H). MS (m/z, I_{rel} %): 353 $[M]^+$ (55), 339 (26), 338 (100), 310 (15), 205 (14), 169 (16), 77 (13). UV/vis (MeCN, λ_{max}) 263, 393. Calcd for $C_{24}H_{23}N_3$: C 81.55; H 6.56; N 11.89. Found: C 81.35; H 6.48; N 11.34.



3a

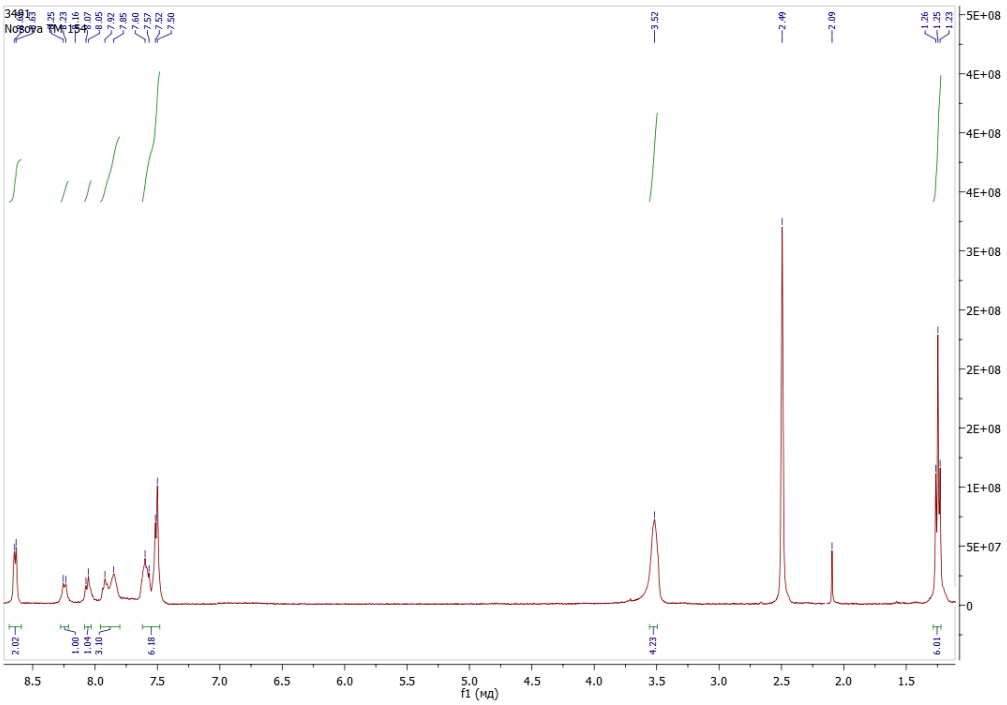


Figure S9. NMR ^{1}H spectrum of quinazoline **3a** in DMSO-d_6.

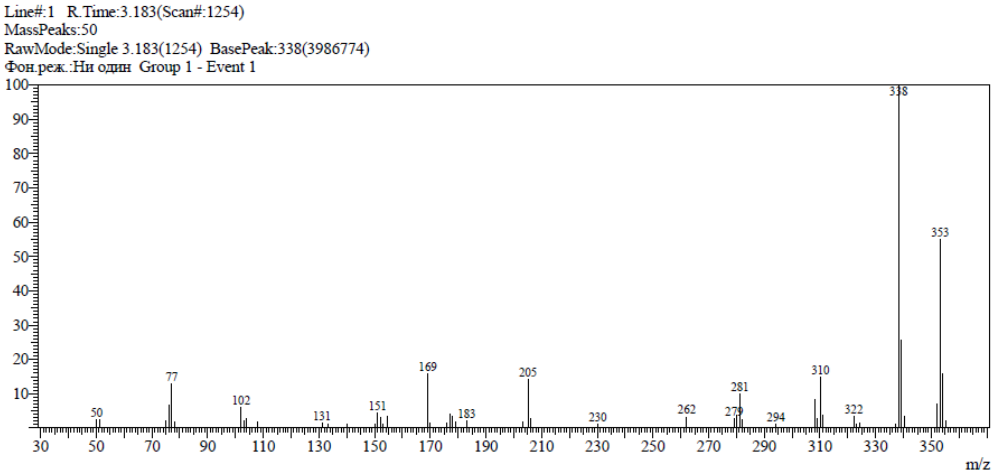
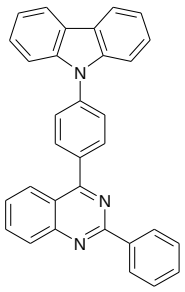


Figure S10. Mass spectrum (EI) of quinazoline **3a.**

Quinazolines **3b-e** were synthesized by similar method.

4-[4-(9*H*-Carbazol-9-yl)phenyl]-2-phenylquinazoline (3b).Yield 80%, mp 197-199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 7.32 (m, 2H, H-2’’’, H-7’’’), 7.46 (m, 2H, H-3’’’, H-6’’’), 7.56 (m, 3H, H-2’, H-3’, H-4’), 7.63 (d, 2H, H-4’’’, H-5’’’, J 8.3 Hz), 7.73 (m, 1H, H-7), 7.92 (d, 2H, H-3’’, H-5’’ J 8.1 Hz), 8.04 (m, 1H, H-6), 8.16-8.22 (m, 5H, H-2’’, H-6’’, H-1’’’, H-8’’’, H-5), 8.34 (d, 1H, H-8, J 8.3 Hz), 8.73 (m, 2H, H-2’, H-6’). MS (m/z, I_{rel} %): 447 $[M]^+$ (100), 446 (40), 281 (52), 282 (12), 224 (14), 76 (10). UV/vis (MeCN, λ_{max}) 238, 259, 291, 339. Calcd for $C_{32}H_{21}N_3$: C 85.88; H 4.73; N 9.39. Found: C 85.47; H 4.82; N 9.50.



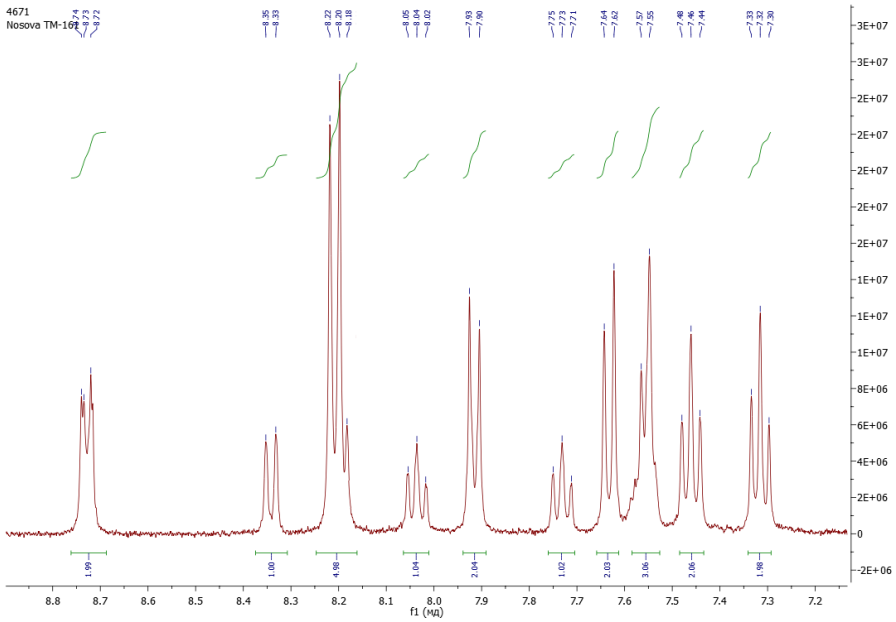


Figure S11. NMR ^{1}H spectrum of quinazoline **3b** in DMSO-d_6.

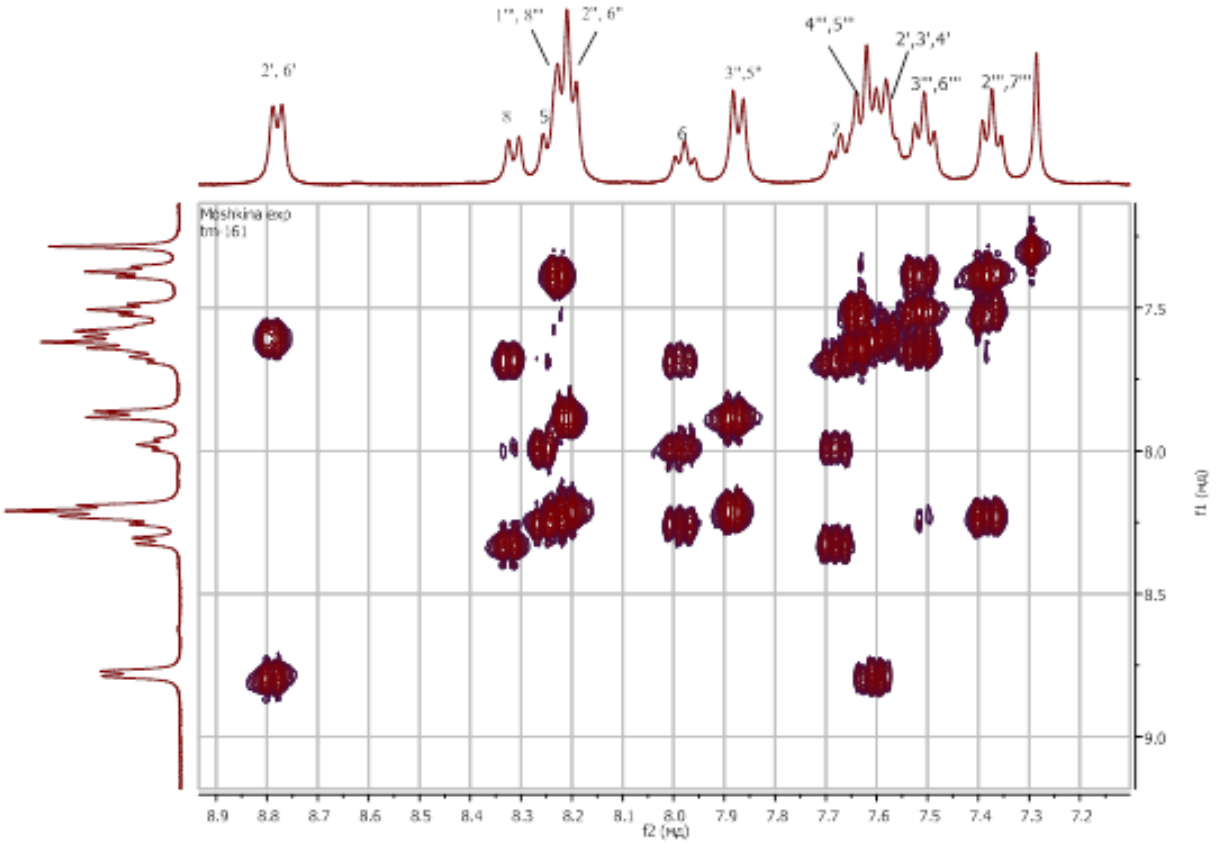


Figure S12. ^{1}H-^{1}H COSY spectrum of quinazoline **3b** in $CDCl_3$.

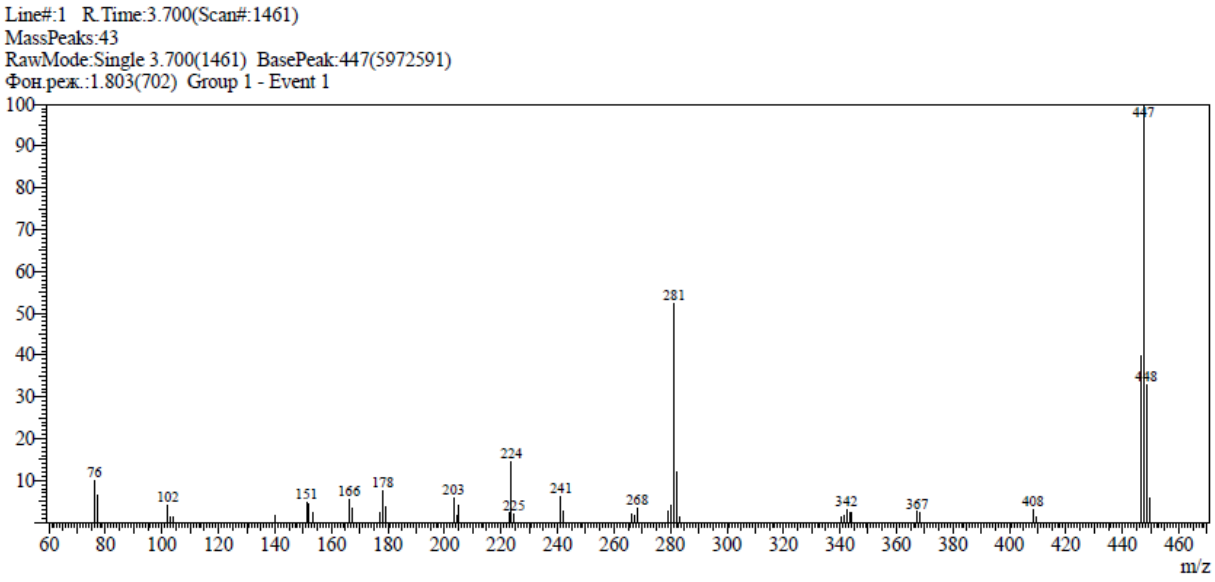
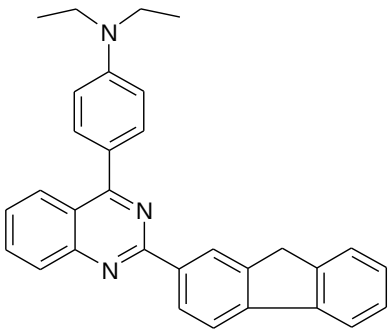


Figure S13. Mass spectrum (EI) of quinazoline **3b.**

4-(4-Diethylaminophenyl)-2-(fluoren-2-yl)quinazoline (3c). Yield 0.09 g (39%), mp 182-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 1,30 (t, 6H, $2CH_3$, J 7,1), 3,52 (q, 4H, $2CH_2$, J 7,1),4,06 (s, 2H, CH_2, флуорен.),6.99 (d, 2H, H-3'', H-5'' J 8.8)7.36 (m, 1H), 7.44 (m, 1H), 7.54(m, 1H), 7.62 (d, 1H, J 7.4), 7.85-7.91 (m, 2H), 7.95 (m, 3H), 8.14 (d, 1H, J 8.4 Hz), 8.32 (d, 1H, J 8.1 Hz), 8.81 (d, 1H, J 8.1 Hz) 8.93 (s, 1H, H-1'). ^{13}C NMR (100 MHz, DMSO-d_6): 12.41, 36.52, 43.85, 111.16, 119.88, 130.47, 120.81, 126.85, 127.26, 128.39, 131.86, 133.61, 136.56, 140.63, 143.32, 143.40, 143.96, 149.05, 151.51, 159.13, 161.20. MS (m/z, I_{rel} %): 441 $[M]^+$ (74), 440 (13), 427 (32), 426 $[M\text{-}CH_3]^+$ (100), 397 (16) $[M\text{-}C_3H_8]^+$, 398 (15), 396 (16), 369 $[M\text{-}NEt_2]^+$ (10), 213 (21), 199 (15), 190 (14), 165 (10). UV/vis (MeCN, λ_{max}) 242, 275, 325, 394. Calcd for $C_{31}H_{27}N_3$: C 84.32; H 6.16; N 9.52. Found: C 84.21; H 6.17; N 9.49.



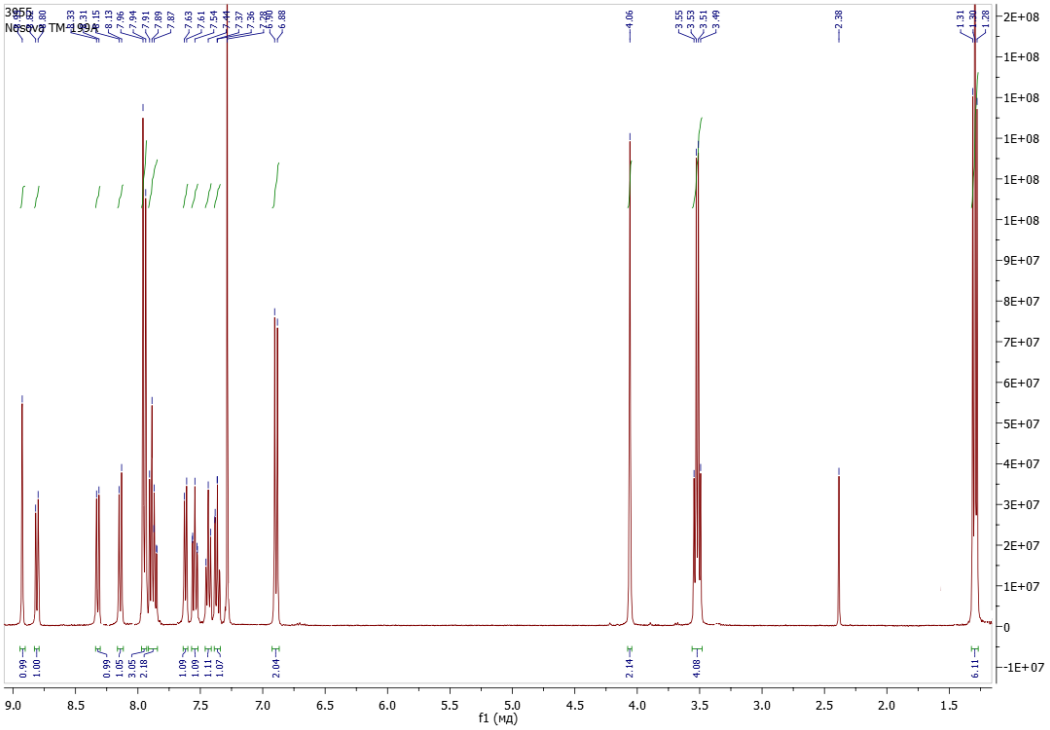


Figure S14. NMR ^{1}H spectrum of quinazoline **3c** in $CDCl_3$.

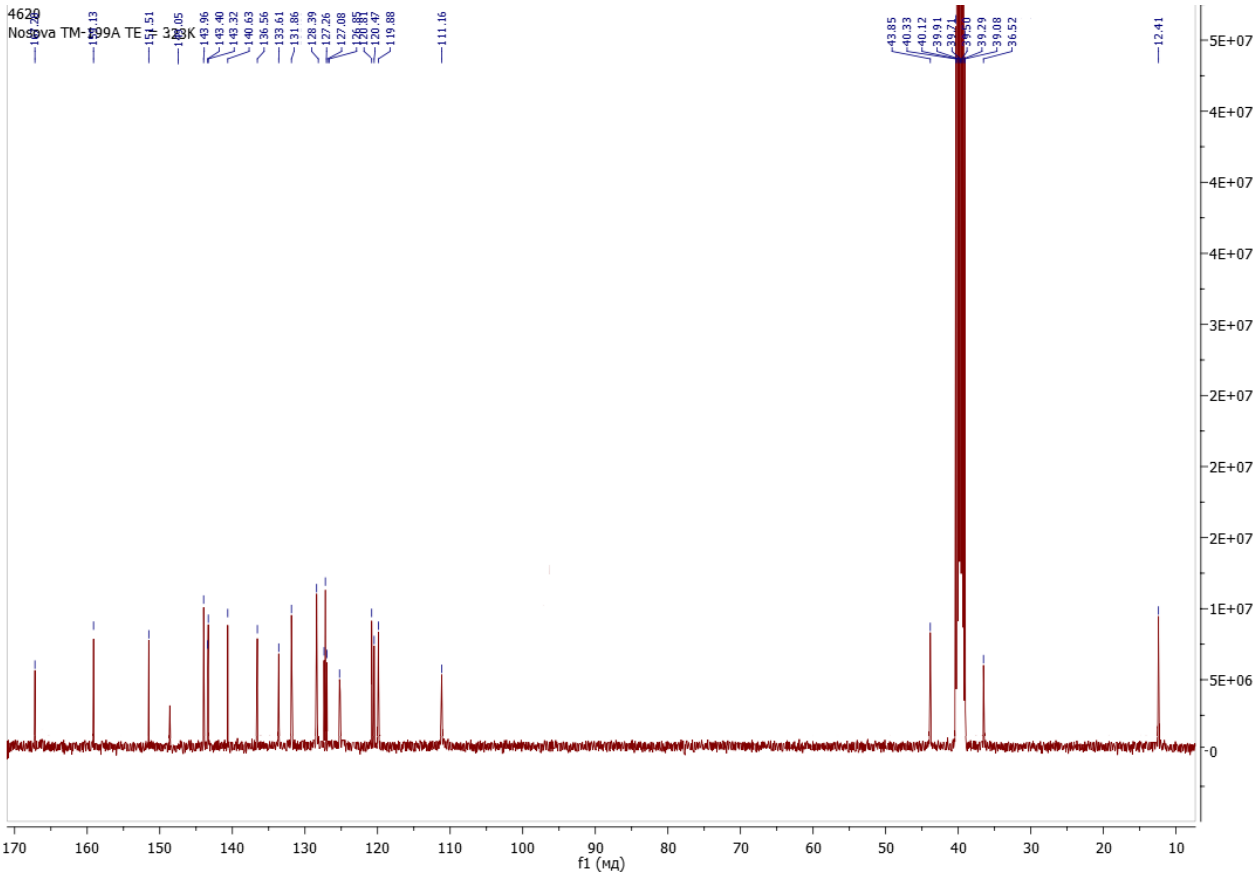


Figure S15. NMR ^{13}C spectrum of quinazoline **3c** in DMSO-d_6.

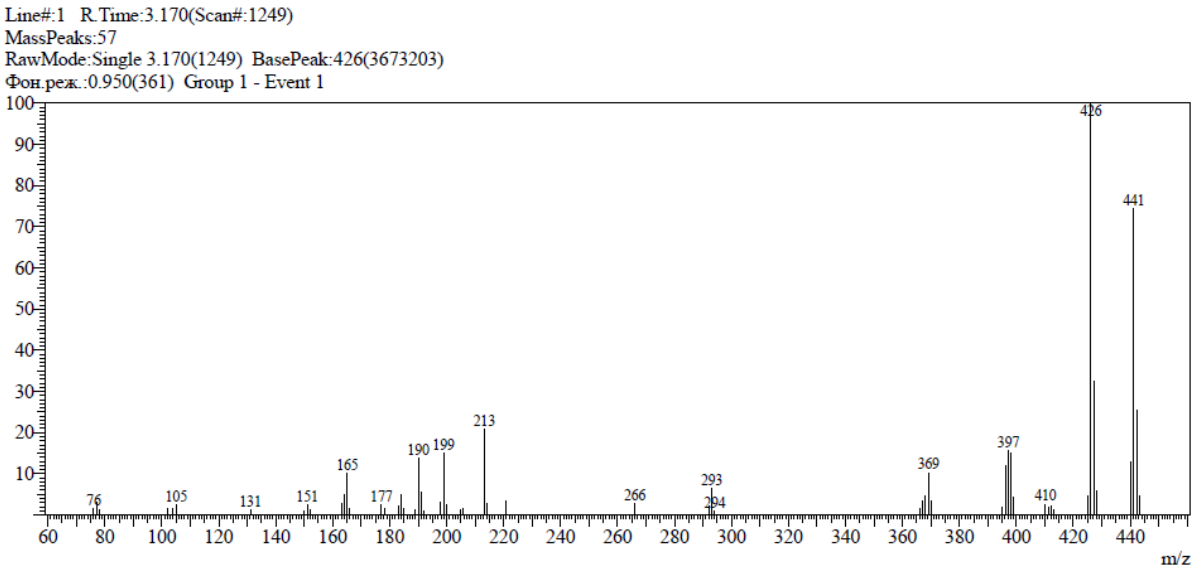


Figure S16. Mass spectrum (EI) of quinazoline **3c.**

4-[4-(9*H*-Carbazol-9-yl)phenyl]-2-(fluoren-2-yl)quinazoline (3d). Yield 0.1 g (34%), mp 260-262 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 4,07 (s, 2H, CH_2),7.30-7.46 (m, 6H), 7.63 (m, 3H), 7.70 (t, 1H, J 7,7), 7.92 (m, 3H), 7.97-8.03 (m, 2H), 8.13-8.23 (m, 5H),8.32 (d, 1H, J 8.4 Hz), 8.79 (d, 1H, J 8.1 Hz), 8.93 (s, 1H, H-1'). MS (m/z, I_{rel} %): 535 $[M]^+$ (100), 534 (32), 369$[M-C_{12}H_{10}N]^+$ (25), 268 (44), 267 (10), 241 (10), 190 (17), 165 (12). UV/vis (MeCN, λ_{max}) 237, 290, 322, 405. Calcd for $C_{39}H_{25}N_3$: C 87.45; H 4.70; N 7.84. Found: C 88.39; H 4.75; N 7.89.

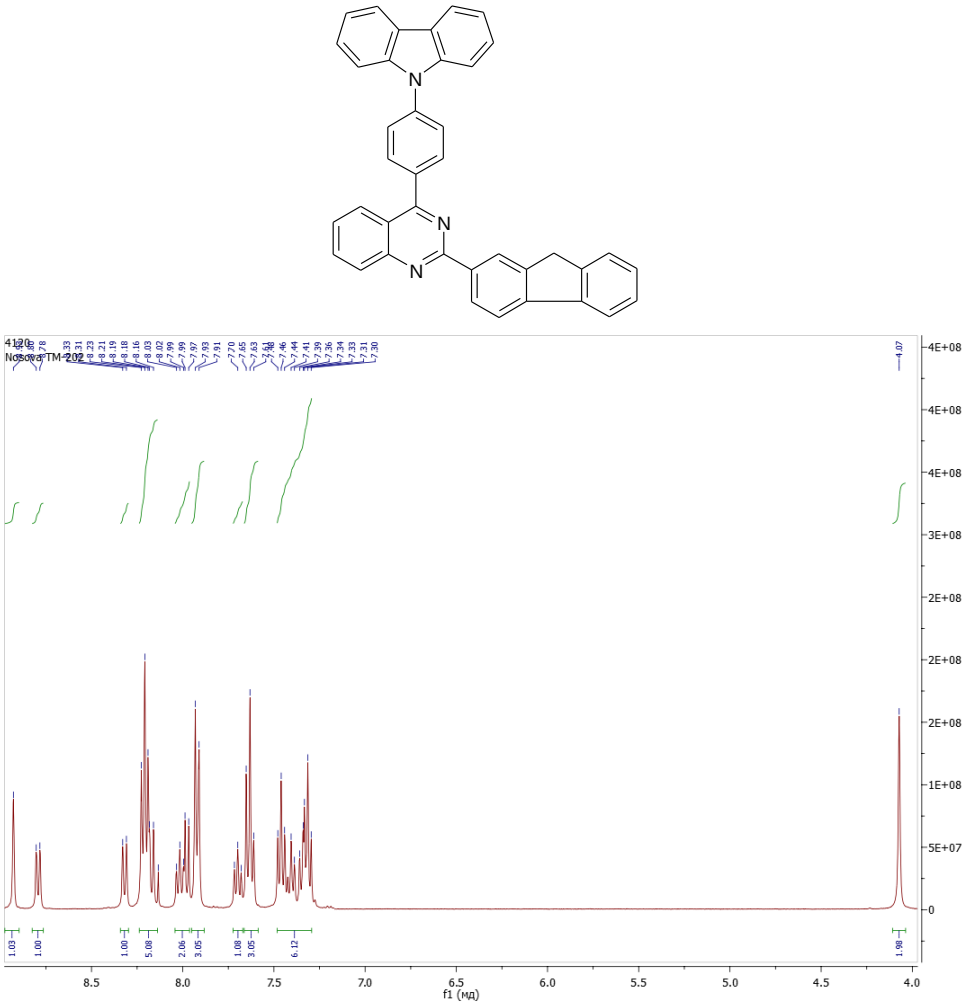


Figure S17. NMR ^{1}H spectrum of quinazoline **3d** in DMSO-d_6.

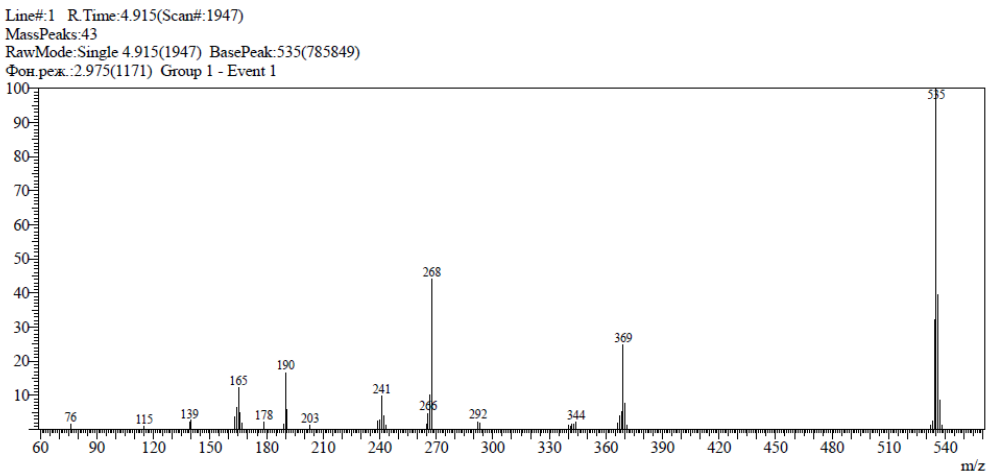
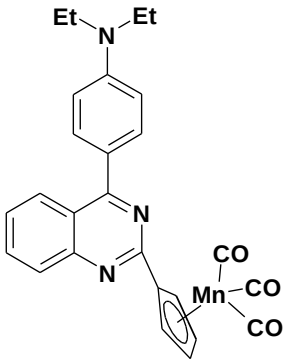


Figure S18. Mass spectrum (EI) of quinazoline **3d.**

4-(4-Diethylaminophenyl)-2-cymantrenylquinazoline (3e). Yield 0.07 g (42 %), mp 125-127 °C. ^{1}H NMR (400 MHz, DMSO-d_6):1.24 (t, 6H, 2CH_3, J 6.9 Hz), 3.49 (m, 4H, 2CH_2), 5.07 (m, 2H, Cp), 5.97 (m, 2H, Cp), 6.83 (m, 2H, H-3', H-5'), 7.58 (m, 1H, arom.), 7.74 (d, 2H, H-2', H-6', J 8.6 Hz), 7.88 (m, 2H, arom.), 7.92 (m, 2H, arom.), 8.22 (m, 1H, H-8). ^{13}C NMR (100 MHz, DMSO-d_6):12.43, 43.76, 84.18, 85.98, 98.42, 110.88, 120.70, 122.49, 127.25, 127.30, 128.01, 131.90, 133.90, 149.14, 151.05, 157.03, 167.07, 224.83 (CO). MS (m/z, I_{rel} %): 479 $[M]^+$ (11), 396 (27), 395 (100), 393 (13), 351 (19), 190 (12). UV/vis (MeCN, λ_{max}) 255, 395. Calcd for $C_{26}H_{22}N_3O_3Mn$: C 65.14; H 4.63; N 8.76. Found: C 65.36; H 4.27; N 8.73.



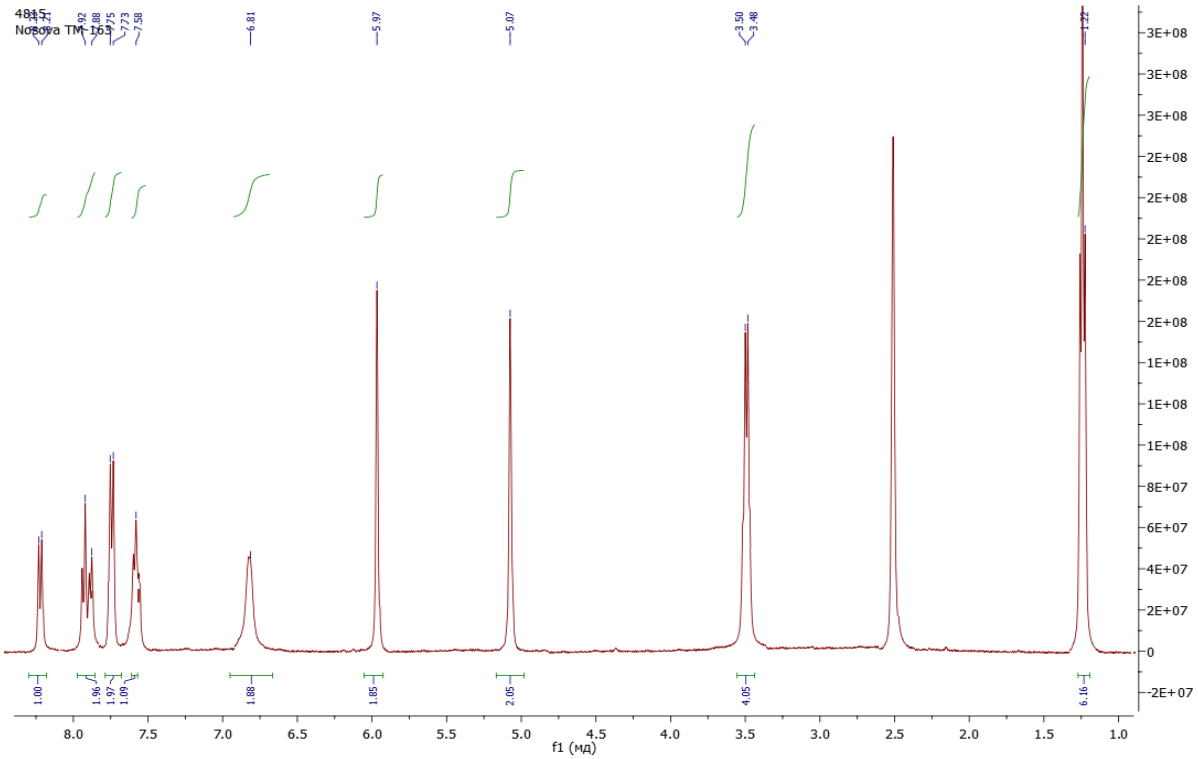


Figure S19. NMR ^{1}H spectrum of quinazoline **3e** in DMSO-d_6.

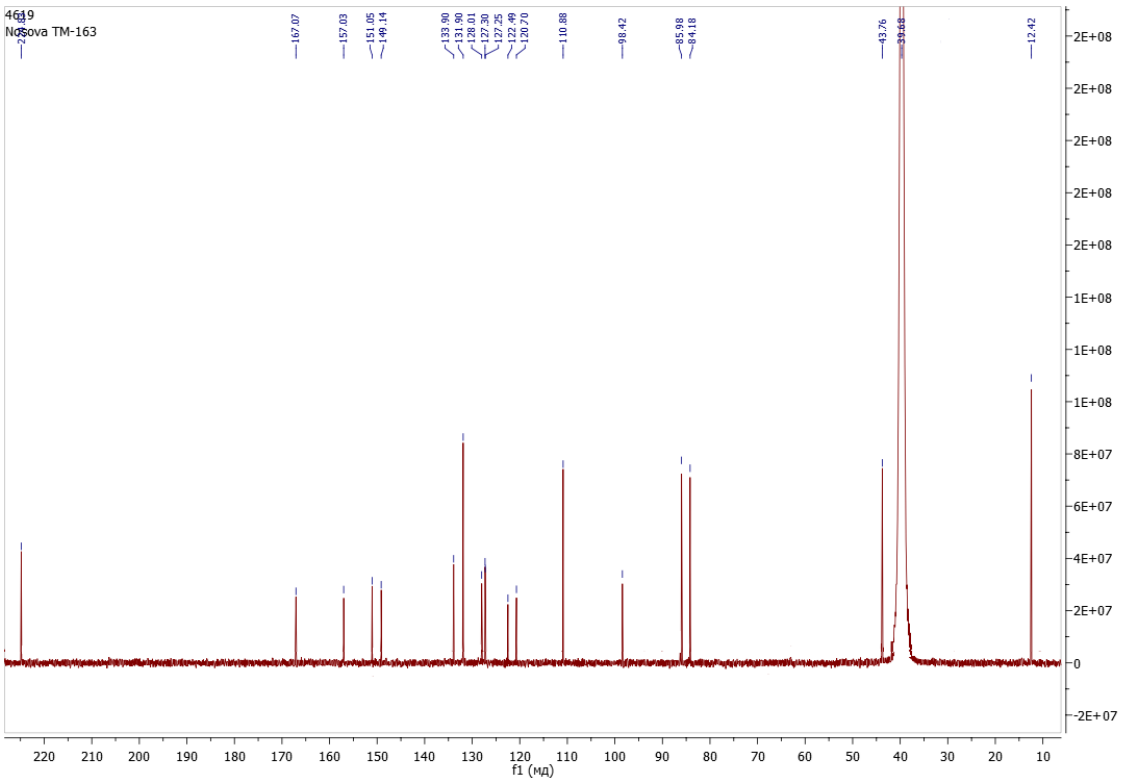


Figure S20. NMR ^{13}C spectrum of quinazoline **3e** in DMSO-d_6.

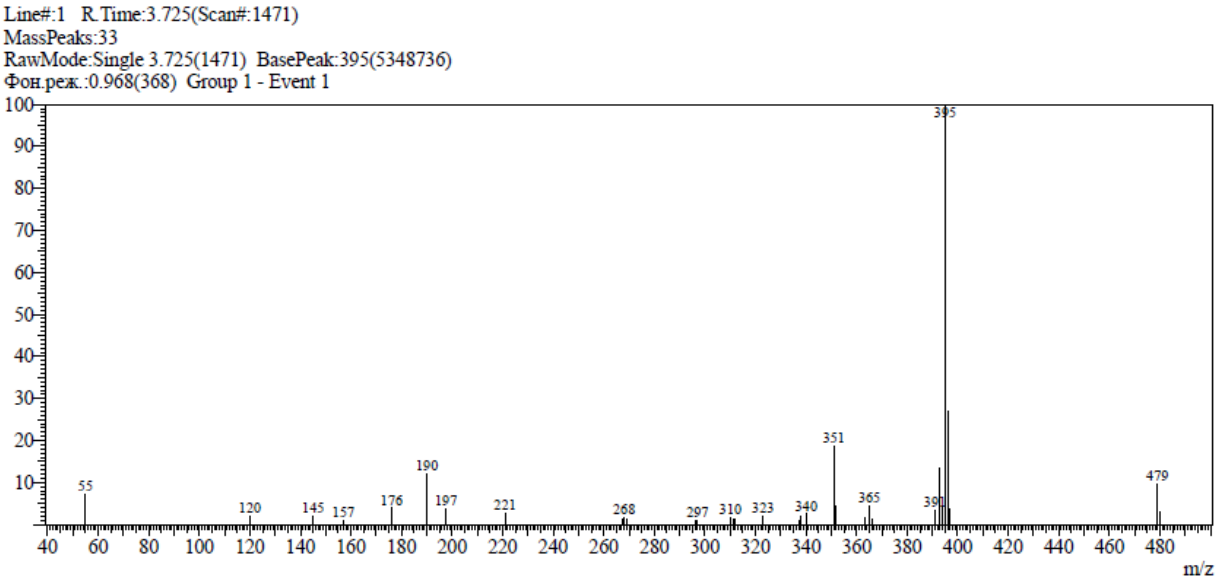


Figure S21. Mass spectrum (EI) of quinazoline **3e.**

Absorption and emission spectra of 2,4-diaryl-substituted quinazolines (3)

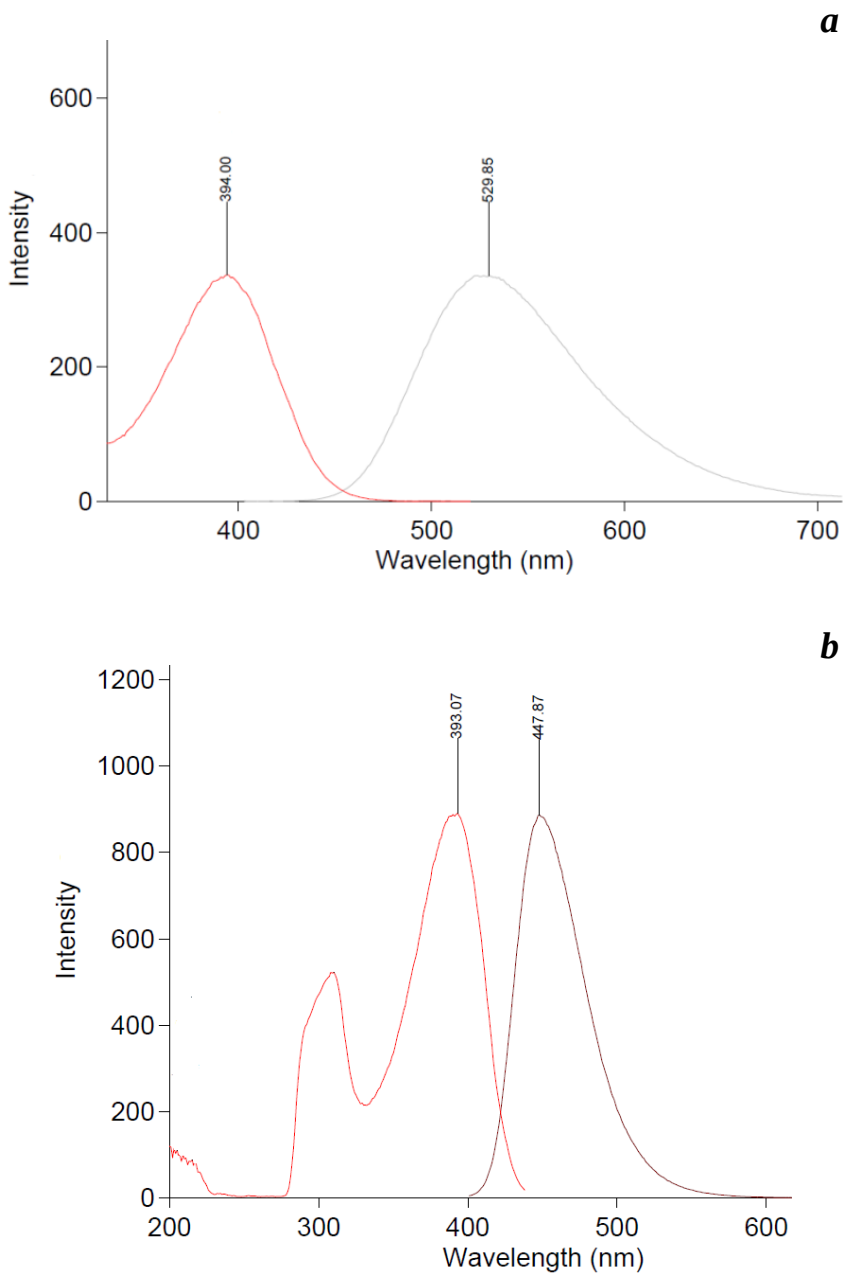


Figure S22. Absorption and emission spectra of quinazoline **3a** in acetonitrile (excitation at 394 nm) (*a*); in toluene (excitation at 391 nm) (*b*).

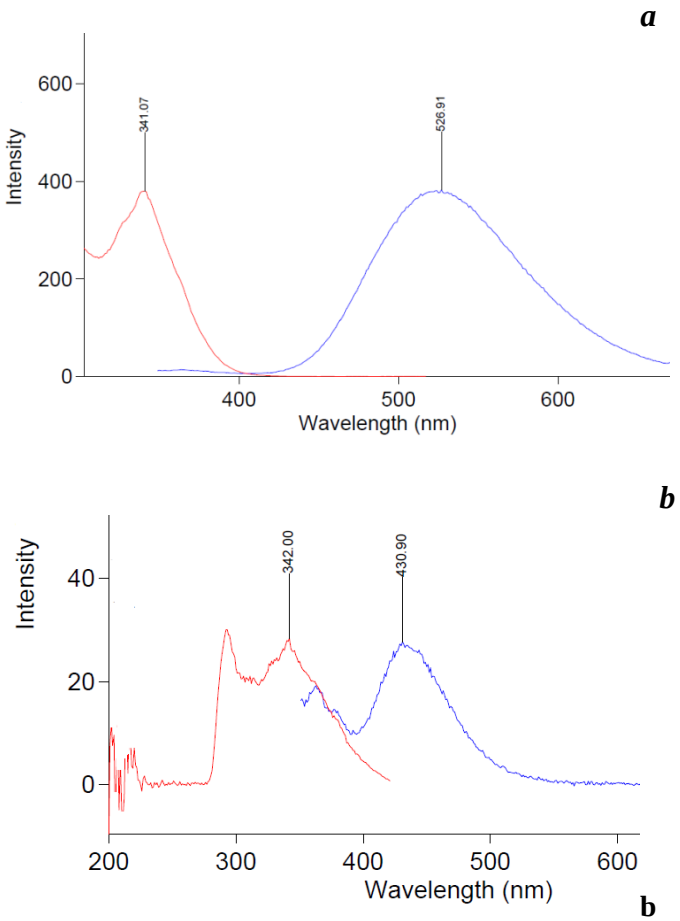


Figure S23. Absorption and emission spectra of quinazoline **3b** in acetonitrile (excitation at 339 nm) (*a*); in toluene (excitation at 341 nm) (*b*).

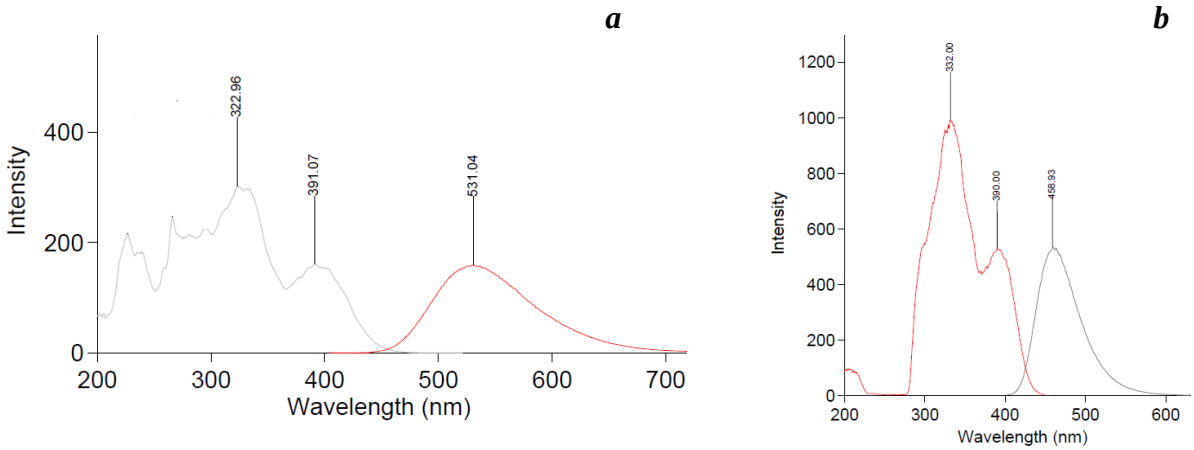


Figure S24. Absorption and emission spectra of quinazoline **3c** in acetonitrile (excitation at 394 nm) (*a*); in toluene (excitation at 392 nm) (*b*).

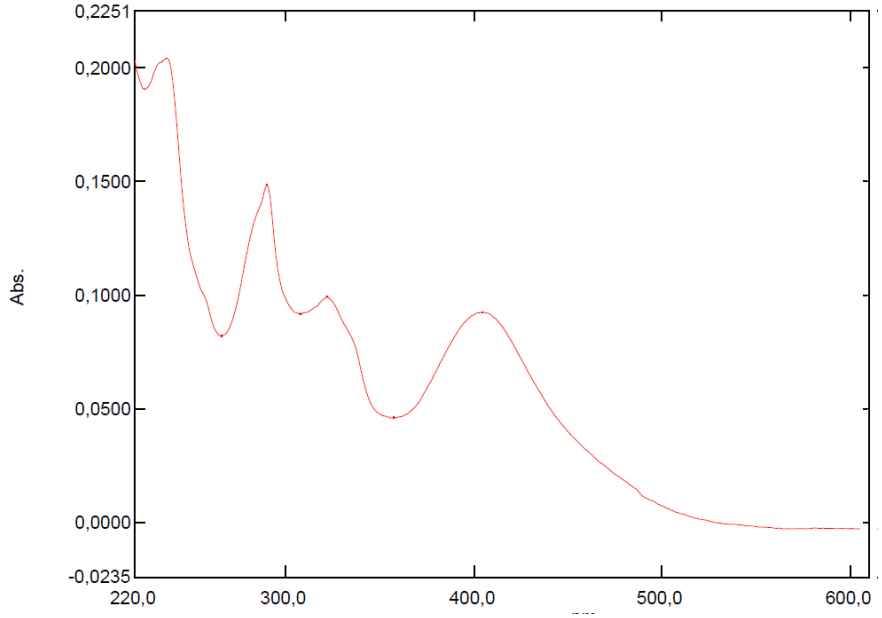


Figure S25. Absorption spectra of quinazoline **3d** in acetonitrile.

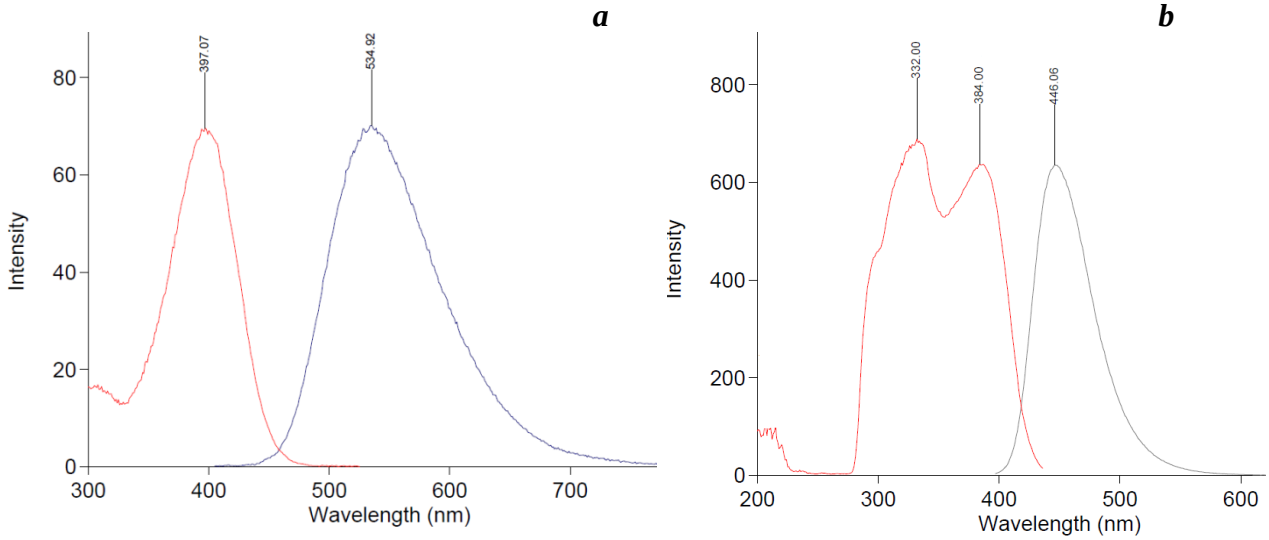


Figure S26. Absorption and emission spectra of quinazoline **3e** in acetonitrile (excitation at 395 nm) (*a*); in toluene (excitation at 387 nm) (*b*).

Table S1. Selected bond lengths of quinazoline **3b**

Bond	Bond length (Å)	Bond	Bond length (Å)
N(1)-C(2)	1.295(7)	C(20)-C(21)	1.361(8)
N(1)-C(10)	1.347(7)	C(21)-C(22)	1.347(7)
N(2)-C(14)	1.409(5)	C(22)-C(23)	1.446(8)
N(2)-C(17)	1.375(6)	C(23)-C(24)	1.360(7)
N(2)-C(28)	1.399(6)	C(23)-C(28)	1.400(7)
C(2)-N(3)	1.372(5)	C(24)-C(25)	1.344(9)
C(2)-C(3)	1.480(7)	C(25)-C(26)	1.407(8)
N(3)-C(4)	1.270(6)	C(26)-C(27)	1.377(7)
C(3)-C(29)	1.378(6)	C(27)-C(28)	1.368(8)
C(3)-C(33)	1.339(7)	C(29)-H(29)	0.931(7)
C(4)-C(5)	1.407(7)	C(29)-C(30)	1.389(7)
C(4)-C(11)	1.490(6)	C(30)-C(31)	1.388(8)
C(5)-C(6)	1.399(7)	C(31)-H(31B)	0.930(8)
C(5)-C(10)	1.441(6)	C(31)-C(32)	1.313(7)
C(6)-C(7)	1.309(9)	C(32)-C(33)	1.362(7)
C(7)-C(8)	1.418(7)	N(1)-C(2)	1.310(8)
C(8)-C(9)	1.343(7)	N(1)-C(10)	1.340(8)
C(9)-C(10)	1.389(7)	N(2)-C(14)	1.404(6)
C(11)-C(12)	1.366(7)	N(2)-C(17)	1.372(7)
C(11B)-C(16B)	1.348(7)	N(2)-C(28)	1.348(6)
C(12)-C(13)	1.385(6)	C(2)-N(3)	1.335(6)
C(13)-C(14)	1.360(7)	C(2)-C(3)	1.465(8)
C(14)-C(15)	1.395(7)	N(3)-C(4)	1.326(7)
C(15)-C(16)	1.388(6)	C(3)-C(29)	1.407(8)
C(17)-C(18)	1.394(7)	C(3)-C(33)	1.331(9)
C(17)-C(22)	1.394(6)	C(4)-C(5)	1.411(8)
C(18)-C(19)	1.345(7)	C(4)-C(11)	1.470(6)
C(19)-C(20)	1.394(7)	C(5)-C(6)	1.405(8)

Table S2. Selected bond angles of quinazoline **3b.**

Angle	(°)	Angle	(°)
C2-N1-C10	117.3(4)	C18-C17-C22	121.6(4)
C14-N2-C17	126.9(4)	C17-C18-C19	117.4(4)
C14-N2-C28	124.5(4)	C18-C19-C20	120.9(5)
C17-N2-C28	108.5(4)	C19-C20-C21	121.2(5)
N1-C2-N3	125.3(4)	C20-C21-C22	119.4(5)
N1-C2-C3	118.8(4)	C17-C22-C21	119.6(4)
N3-C2-C3	115.9(4)	C17-C22-C23	107.2(4)
C2-N3-C4	118.8(4)	C21-C22-C23	133.3(5)
C2-C3-C29	118.8(4)	C22-C23-C24	134.1(5)
C2-C3-C33	122.7(4)	C22-C23-C28	106.3(4)
C29-C3-C33	118.5(4)	C24-C23-C28	119.5(5)
N3-C4-C5	122.5(4)	C23-C24-C25	120.5(5)
N3-C4-C11	116.6(4)	C24-C25-C26	120.7(6)
C5-C4-C11	120.9(4)	C25-C26-C27	119.4(5)
C4-C5-C6	127.8(4)	C26-C27-28	119.0(5)
C4-C5-C10	115.0(4)	N2-C28-C23	108.7(4)
C6-C5-C10	116.9(4)	N2-C28-C27	130.5(4)
C5-C6-C7	122.2(5)	C23-C28-C27	120.7(5)
C6-C7-C8	121.1(6)	C3-C29-C30	119.3(4)
C7-C8-C9	119.3(5)	C29-C30-C31	120.2(5)
C8-C9-C10	121.2(4)	C30-C31-C32	118.4(5)
N1-C10-C5	121.0(4)	C31-C32-C33	122.0(5)
N1-C10-C9	119.9(4)	C3-C33-C32	121.6(4)
C5-C10-C9	119.1(4)	C2-N1-C10	118.5(5)
C4-C11-C12	118.0(4)	C14-N2-C17	123.9(4)
C4-C11-C16	121.2(4)	C14-N2-C28	127.7(4)
C12-C11-C16	120.8(4)	C17-N2-C28	108.4(4)
C11-C12-C13	118.9(4)	N1-C2-N3	125.1(5)
C12-C13-C14	120.9(4)	N1-C2-C3	119.4(5)
N2-C14-C13	119.9(4)	N3-C2-C3	115.5(4)
N2-C14-C15	120.1(4)	C2-N3-C4	117.5(4)
C13-C14-C15	119.9(4)	C2-C3-C29	119.1(5)
C14-C15-C16	118.0(4)	C2-C3-C33	121.1(5)
C11-C16-C15	121.2(4)	N3-C4-C5	122.1(4)
N2-C17-C18	129.1(4)	N3-C4-C11	114.9(4)
N2-C17-C22	109.2(4)	C5-C4-C11	122.9(4)